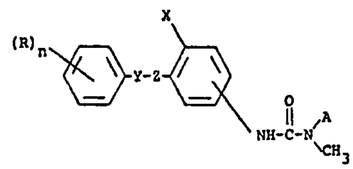
(12) UK Patent Application (19) GB (11) 2 016 010 A

(21) Application No 7908549
(22) Date of filing
12 Mar 1979
(23) Claims filed
12 Mar 1979
(30) Priority data
(31) 53/028897
(32) 13 Mar 1978
(33) Japan (JP)
(43) Application published
19 Sep 1979
(51) INT CL² C07C 127/19
A01N 9/12 9/20
C07C 119/048
149/437
C07D 317/64
(52) Domestic classification
C2C 1494 213 220 227 22Y 253 25Y 276 281 30Y 311 313 314 31Y 326 338 341 342 345 349 34Y 364 36Y 373 37Y 591 613 622 624 626 62X 634 662 672 694 697 699 714 71X 805 80Y KD KR MH RB RC
(56) Documents cited
GB 1079205
GB 913383
(58) Field of search
C2C

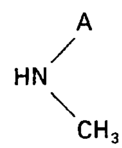
(71) Applicant
Sumitomo Chemical Company Limited
No 15 Kitahama 5-chome
Higashi-ku
Osaka-shi
Osaka-fu
Japan
(72) Inventors
Ryo Yoshida
Ichiki Takemoto
Seizo Sumida
Katsuzo Kamoshita
(74) Agents
Boult Wade & Tennant

(54) N'-phenyl-N-methylurea derivatives

(57) Compounds of the formula:



wherein A is hydrogen, methyl or methoxy, each of the Rs is independently a halogen atom or a lower alkyl, lower alkoxy, lower alkylthio, trifluoromethyl, cyano or methylenedioxy group, X is a hydrogen or halogen atom, Y is an oxygen or sulfur atom, Z is a lower alkylene group and n is from 0 to 3, provided that the substituted ureido group is present at the m- or p-position to the substituent X and at the m- or p-position to the substituent Z; are useful as selective herbicides and fungicides. They can be prepared, for example, by reacting the corresponding *phenyl isocyanate* with a reagent of the formula:



or, when A is methoxy, by methylating the corresponding *1-hydroxy urea derivative.*

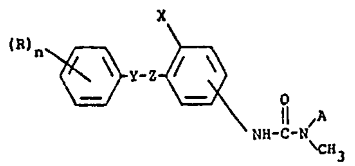
GB 2 016 010 A

SPECIFICATION

N′-phenyl-N-methylurea derivatives, and their production and use

The present invention relates to N′-phenyl-N-methylurea derivatives, and their production and use.

The N′-phenyl-N-methylurea derivatives of the present invention are representable by the formula:



(I)

wherein A is a hydrogen atom, a methyl group or a methoxy group, the Rs are same as or different from each other and each is a halogen atom (preferably chlorine, bromine or fluorine), a lower alkyl group (e.g. methyl, ethyl, propyl, isopropyl or butyl), a lower alkoxy group (e.g. methoxy or ethoxy), a lower alkylthio group (e.g. methylthio), a trifluoromethyl group, a cyano group or a methylenedioxy group, X is a hydrogen atom or a halogen atom (preferably chlorine), Y is an oxygen atom or a sulfur atom, Z is a lower alkylene group (e.g. methylene, ethylene, propylene or trimethylene) and n is an integer of 0 to 3.

In the above formula (I), the substituted ureido group is present at the m- or p-position to the substituent represented by the symbol X and at the same time at the m- or p-position to the substituent represented by the symbol Z. The term "lower" is intended to mean a group having 1 to 5 carbon atoms. The preferred number of the carbon atoms is from 1 to 4 for "lower" alkyl and 1 or 2 for "lower" alkoxy.

Soybeans, peanuts, cotton, corn, wheat, rice, sugar beet and the like are crops of world-wide importance and, in the cultivation of these crops, chemical control of weeds is necessary to prevent reductions in the yield.

Among substituted urea derivatives, as is well known, there are compounds having a strong herbicidal activity, such as N′-4-chlorophenyl-N,N-dimethylurea (monuron) and N′-3,4-dichlorophenyl-N,N-dimethylurea (diuron). It is also well known that the herbicidal activity of these urea derivatives is due to the inhibition of photosynthesis. Photosynthesis is a physiological function peculiar to higher plants and does not take place in mammals. Accordingly, specific inhibitors of the photosynthetic process usually cause no significant harm to mammals but can be extremely effective in the extermination of higher plants. In fact, herbicidal photosynthesis inhibitors such as monuron, diuron, 5-bromo-3-sec-butyl-6-methyluracil (bromacil) and the like are all low in mammalian toxicity. However, they exert a herbicidal activity against all higher plants, i.e. crops and weeds alike, since photosynthesis is common to all of the higher plants. Most photosynthesis inhibitors are non-selective and damage crop plants.

A compound to be a selective herbicide should have both a strong herbicidal activity against weeds and a high level of selectivity to the intended crop. However, such selective herbicides are very difficult to find and can not easily be predicted by mere analogy and modification of known chemical structures. Therefore, a highly detailed study with trial and error is necessary to find such selective herbicides. Selective herbicidal activity requires a very specific chemical structure, and only a slight difference in the chemical structure can produce quite a large difference in the degree and kind of selectivity.

It has now been found that the compounds of the formula (I) show a remarkable herbicidal activity with no phytotoxicity to rice plants in paddy field by soil treatment after transplantation. Besides, they can safely be used in upland field without phytoxicity to rice plant, wheat, corn, soybeans, peanuts, cotton and sugar beet by pre-emergence application. The compounds of the present invention may be used as foliar-applied herbicides which can safely be applied to said crop plants including wheat and soybeans. When the compounds (I) are applied to soybean field as a foliar-applied agent, they can exterminate many weeds such as large crabgrass (*Digitaria sanguinalis*), cocklebur (*Xanthium pensylvanicum*), annual morningglory (*Ipomoea purpurea*), jimsonweed (*Datura stramonium*), sunflower (*Helianthuc annuus*), and redroot pigweed (*Amaranthus retroflexus*), with little phytotoxicity to soybeans.

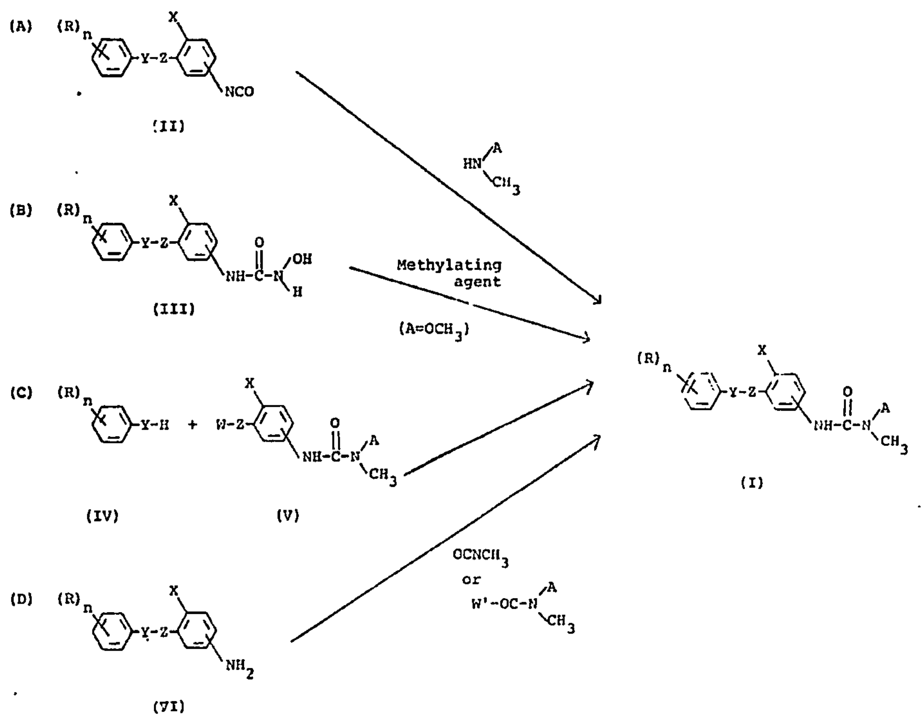
As described above, the compounds (I) are very useful as selective herbicides for crop lands and besides they can be used as excellent herbicides for non-crop land on account of their strong herbicidal activity.

In addition, it may be noted that the compounds (I) are effective in prevention and inhibition of plant diseases caused by various phytopathogenic fungi in crop plants and fruit trees such as powdery mildew in apples, pears, grapes, oranges, cucumbers, melons, wheat, etc., downy

mildew in grapes, oranges, cucumbers, melons, etc., yellows in root crops and rust in wheats, beans, etc. They are particularly effective in prevention and inhibition of rust such as stripe rust in barleys and wheats caused by *Puccinia striiformis*, stem rust in barleys and wheats caused by *Puccinia graminis*, leaf rust in wheats caused by *Puccinia recondita*, crown rust in oats caused by *Puccinia coronata*, rust in soybeans caused by *Uromyces sojae* and rust in kidney beans caused by *Uromyces appendiculatus*. Compared with conventional fungicides, the compounds (I) are characteristic in having not only a preventative effect but also a curative effect.

Accordingly, the compounds (I) of the present invention are useful as herbicides and/or fungicides. Particularly when they are used in cultivation of paddy rice plant, upland rice plant, cotton, soybeans, corn, wheat, barley, etc., simultaneous herbicidal and fungicidal effects can be expected.

The compounds (I) are novel and can be produced, for instance, by the procedures as shown in the following scheme:



wherein W and W' are each a halogen atom (e.g. chlorine, bromine) and A, R, X, Y, Z and n are each as defined above.

Procedure (A)

The compound (I) may be obtained by reacting the phenyl isocyanate (II) with a reagent of the formula:

$$HN\begin{matrix}\diagup A \\ \diagdown CH_3\end{matrix} \qquad (I)$$

(I)

wherein A is as defined above.

The reaction may be carried out in an organic solvent (e.g. benzene, toluene, xylene, diethyl ether, tetrahydrofuran, dioxane, N,N-dimethylformamide, chloroform, carbon tetrachloride), water or mixture thereof. The regent (1) is used ordinarily in an amount of 1 to 3 mole, preferably in an amount of 1 to 1.5 mole, to 1 mole of the phenyl isocyanate (II). The reaction is effected usually at a temperature of 0 to 50°C and comes to an end in 1 to 10 hours.

Procedure (B)

The compound (I) wherein A is methoxy may be obtained by reacting the hydroxyurea (III) with a methylating agent.

In the reaction, the methylating agent is normally employed in an amount of 2 to 6 mole, preferably in an amount of 2 to 4 mole, to the hydroxyurea (III). As the methylating agent, there may be used methyl iodide, dimethyl sulfate, diazomethane or the like. When dimethyl sulfate is used, for example, the reaction may be carried out in a solvent in the presence of an alkali. Examples of the alkali are sodium hydroxide and potassium hydroxide, and examples of the solvent are organic solvents (e.g. benzene, toluene, xylene, methanol, ethanol, isopropanol, diethyl ether, tetrahydrofuran, dioxane, methylene chloride), water and mixtures thereof. The existence of a phase transfer catalyst such as a quaternary ammonium salt (e.g. benzyltriethylammonium chloride, tetra-n-butylammonium bromide) in the reaction system is favorable for attaining a better result. The reaction is effected usually at a temperature of 0 to 100°C and comes to an end in 1 to 10 hours.

Procedure (C)

The compound (I) may be obtained by reacting the (thio)phenol (IV) with the phenylalkyl halide (V).

In the reaction, the (thio)phenol (IV) and the phenylalkyl halide derivative (V) is usually employed in a molar proportion of 1–3:1, preferably of 1–1.5:1. The reaction may be carried out in an inert organic solvent (e.g. benzene, toluene, xylene, diethyl ether, tetrahydrofuran, dioxane, chloroform, carbon tetrachloride, methylene chloride, ethyl acetate, N,N-dimethylformamide) or water, or their mixture in the presence of a dehydrohalogenating agent (e.g. pyridine, triethylamine, sodium hydroxide, potassium hydroxide, sodium carbonate). The reaction is effected usually at a temperature of 0 to 120°C and comes to an end in 0.5 to 10 hours.

Procedure (D)

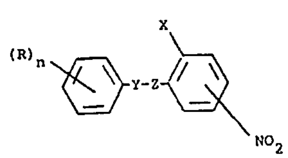
The compound (I) may be obtained by reacting the aniline (VI) with a reagent selected from the group consisting of methyl isocyanate, N,N-dimethylcarbamyl halide and N-methoxy-N-methylcarbamyl halide.

In the reaction, the reagent is normally used in an amount of 1 to 3 mole, preferably in an amount of 1 to 1.5 mole, to 1 mole of the aniline (VI). The reaction may be carried out in an inert organic solvent (e.g. benzene, toluene, xylene, diethyl ether, tetrahydrofuran, dioxane, chloroform, carbon tetrachloride, methylene chloride, ethyl acetate, N,N-dimethylformamide), in case of the reagent being N,N-dimethylcarbamyl halide or N-methoxy-N-methylcarbamyl halide, in the presence of a dehydrohalogenating agent (e.g. pyridine, triethylamine, sodium hydroxide, potassium hydroxide, sodium carbonate). The reaction is effected usually at a temperature of 0 to 150°C for 1 to 30 hours.

In the above procedures, the phenyl isocyanate (II) may be prepared by reacting the aniline (VI) with phosgene. In the reaction, phosgene is employed usually in an amount of 1 to 5 mole, favorably of 1 to 3 mole, to 1 mole of the aniline (VI). The reaction is normally carried out in an inert organic solvent (e.g. benzene, toluene, xylene, tetrahydrofuran, dioxane, chloroform, carbon tetrachloride, ethyl acetate) at room temperature (about 20°C) to the reflux temperature of the solvent and the reaction may take from only a moment to 10 hours.

The hydroxyurea (III) can be obtained by reacting the phenyl isocyanate (II) with hydroxylamine. In the reaction, the phenyl isocyanate (II) and hydroxylamine are usually employed in a molar proportion of 1:1–3, preferably of 1:1–1.5. The reaction is ordinarily carried out in an organic solvent (e.g. benzene, toluene, xylene, diethyl ether, tetrahydrofuran, dioxane, chloroform, carbon tetrachloride) or water, or their mixture at a temperature of 0 to 50°C and may take from only a moment to 30 hours.

The aniline (VI) is obtainable by reduction of the corresponding nitrobenzene of the formula:

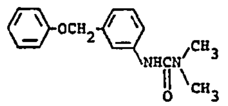
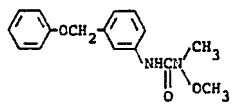
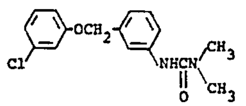
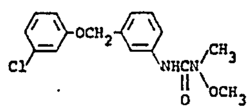
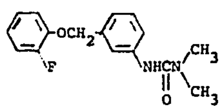
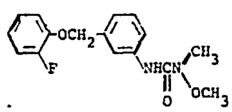
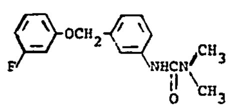
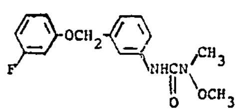
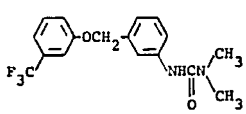
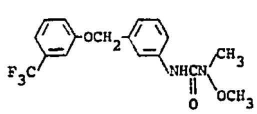
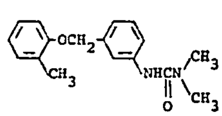
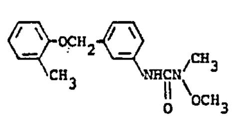
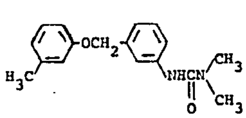
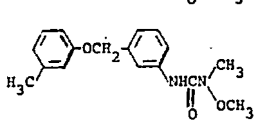


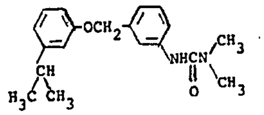
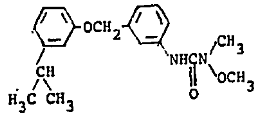
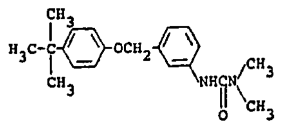
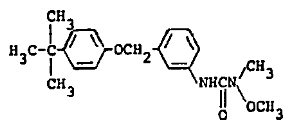
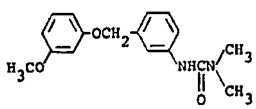
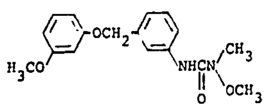
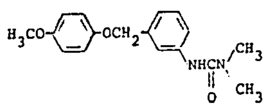
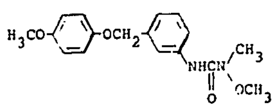
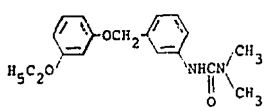
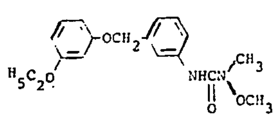
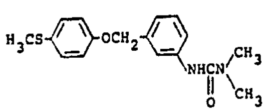
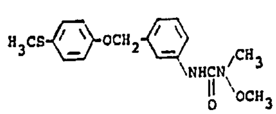
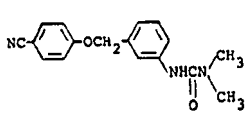
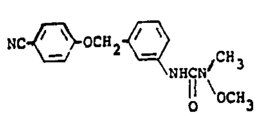
(VII)

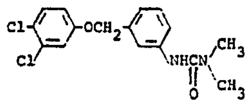
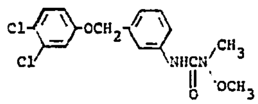
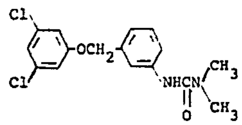
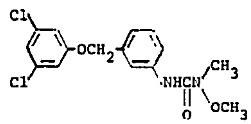
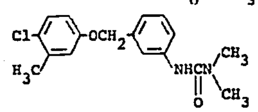
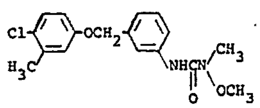
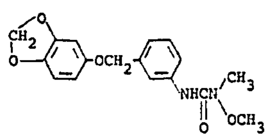
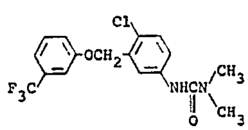
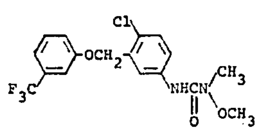
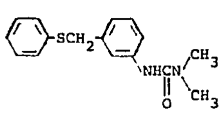
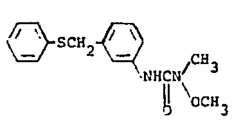
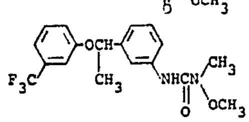
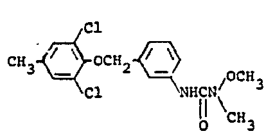
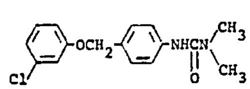
wherein R, X, Y, Z and n are each as defined above, the latter being prepared by the method as disclosed in J.A.C.S., *70*, 2310–2313 (1948).

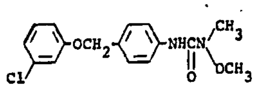
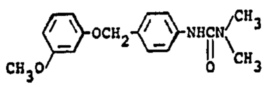
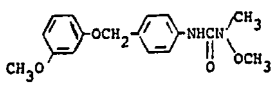
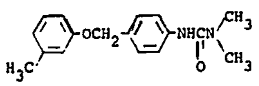
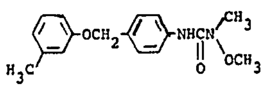
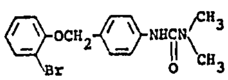
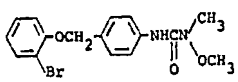
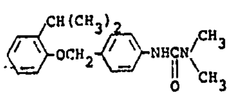
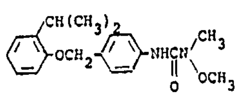
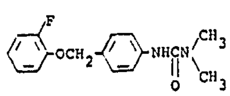
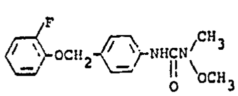
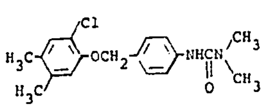
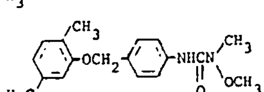
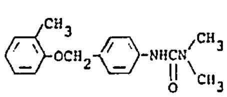
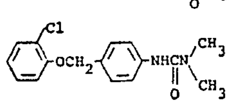
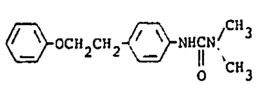
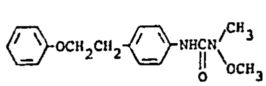
The following patents also disclose compounds, which are more or less structurally related to the compounds (I) of the invention, and their production: U.S. patent 4,123,256 issued October 31, 1978; U.S. patent 4,129,436 issued December 12, 1978; U.S. patent 4,144,049 issued March 13, 1979.

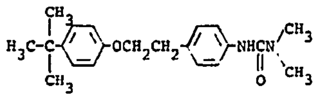
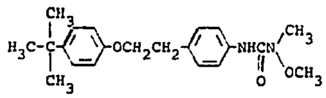
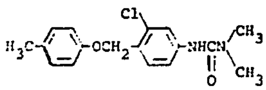
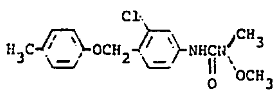
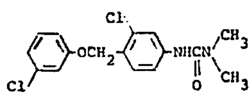
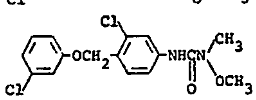
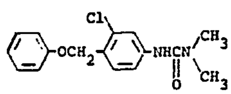
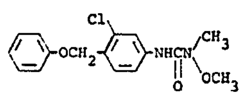
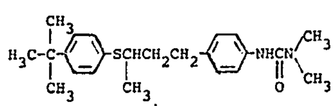
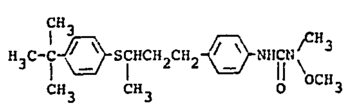
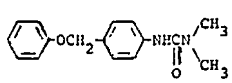
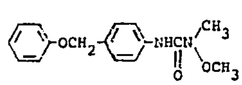
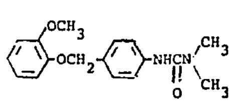
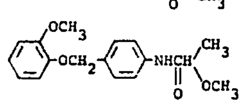
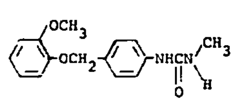
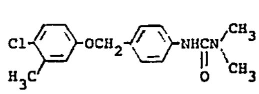
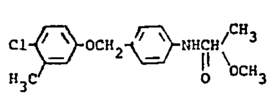
Examples of the compound (I) of the invention are shown below.

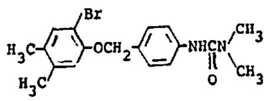
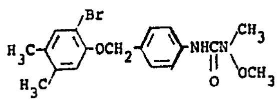
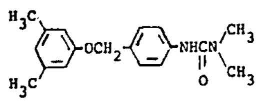
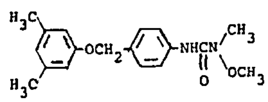
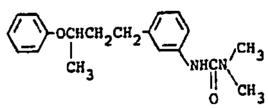
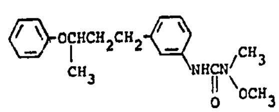
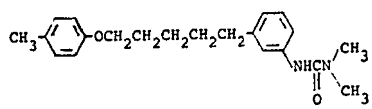
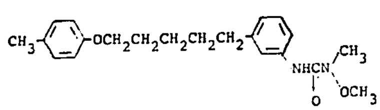
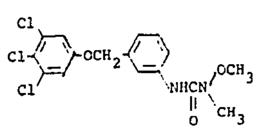
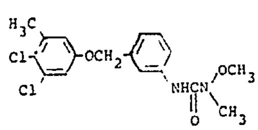
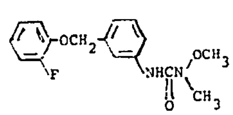
Compound No.	Chemical structure	Melting point or refractive index
1		M.P., 128.5-130°C
2		M.P., 72.5-73°C
3		M.P., 127-129°C
4		M.P., 83-84°C
5		M.P., 113.5-115°C
6		M.P., 87-88°C
7		M.P., 123-124.5°C
8		M.P., 71-72.5°C
9		M.P., 111-112°C
10		M.P., 102-103°C
11		M.P., 131.5°C
12		M.P., 92°C
13		M.P., 128°C
14		M.P., 83°C

Compound No.	Chemical structure	Melting point or refractive index
15		M.P., 100.5-103°C
16		M.P., 67-68°C
17		M.P., 144.5-147°C
18		M.P., 85-86°C
19		M.P., 135-136.5°C
20		M.P., 76-79.5°C
21		M.P., 130.5-131°C
22		M.P., 77-80°C
23		M.P., 129-131°C
24		M.P., 70.5-71.5°C
25		M.P., 150.5-153.5°C
26		M.P., 68.5-69.5°C
27		M.P., 134.5-136°C
28		M.P., 117.5-119.5°C

Compound No.	Chemical structure	Melting point or refractive index
29		M.P., 143-145°C
30		M.P., 102-104°C
31		M.P., 150.5-152.5°C
32		M.P., 105.5-106.5°C
33		M.P., 135-135.5°C
34		M.P., 104-105.5°C
35		M.P., 84-85.5°C
36		M.P., 122-123.5°C
37		M.P., 92.5-94°C
38		M.P., 159-161°C
39		M.P., 106.5-107°C
40		M.P., 112-113.5°C
41		M.P., 93-94°C
42		M.P., 109-110°C

Compound No.	Chemical structure	Melting point or refractive index
43		M.P., 68-70°C
44		M.P., 85-86°C
45		M.P., 76-79°C
46		M.P., 135-136°C
47		M.P., 101-102°C
48		M.P., 106-108°C
49		n_D^{20} 1.5782
50		M.P., 103-104°C
51		n_D^{20} 1.5569
52		M.P., 142.5-143°C
53		M.P., 117-118°C
54		M.P., 93-94°C
55		M.P., 144-146°C
56		M.P., 171-177°C
57		M.P., 136-138°C
58		M.P., 113-115°C
59		n_D^{19} 1.661

Compound No.	Chemical structure	Melting point or refractive index
60		M.P., 112-118°C
61		n_D^{23} 1.6535
62		M.P., 138-139°C
63		M.P., 103-107°C
64		M.P., 132-133°C
65		M.P., 103-104°C
66		M.P., 152-153°C
67		M.P., 100-101°C
68		$n_D^{20.5}$ 1.5746
69		$n_D^{20.5}$ 1.5716
70		M.P., 138-139°C
71		M.P., 114-115°C
72		M.P., 128-130°C
73		M.P., 112-113°C
74		M.P., 167-168°C
75		M.P., 118.5-119°C
76		M.P., 116.5-117°C

Compound No.	Chemical structure	Melting point or refractive index
77		M.P., 132.5-133°C
78		M.P., 89.5-90°C
79		M.P., 149.5-150°C
80		M.P., 134.5-135°C
81		$n_D^{24.0}$ 1.6601
82		$n_D^{21.0}$ 1.5444
83		M.P., 83-84.5°C
84		M.P., 97.0-97.5°C
85		M.P., 136.5-138°C
86		M.P., 121-128°C
87		M.P., 87-88°C

The production of the compound (I) according to the invention are illustratively shown by the following Examples.

Example 1 (Procedure (A))

To a solution of m-(m-methylphenoxymethyl)phenyl isocyanate (23.9 g) in benzene (100 ml) was added dropwise a solution of N,O-dimethylhydroxylamine (7.3 g) in benzene (50 ml) at a temperature below 30°C. The reaction mixture was allowed to stand at room temperature for 2 hours, and the solvent was removed under reduced pressure. The residue was recrystallized from methanol to obtain 23.3 g of N'-m-(m-methylphenoxymethyl)phenyl-N-methoxy-N-methylurea (Compound No. 14) as white needles. M.P., 83°C.

Elementary analysis: Calcd. for $C_{17}H_{20}N_2O_3$: C, 67.98 %; H, 6.71 %; N, 9.33 %. Found: C, 67.81 %; H, 6.85 %; N, 9.26 %.

NMR$\delta CDCl_3$: 2.30 (s, 3H), 3.11 (s, 3H), 3.68 (s, 3H), 4.94 (s, 2H), 6.50–7.40 (8H), 7.65 (s, 1H).

Example 2 (Procedure (B))

To a solution of N'-m-(m-methoxyphenoxymethyl)phenyl-N-hydroxyurea (30.0 g) in a benzene/methanol (1:1) mixture (150 ml), there were alternatively added portionwise dimethyl sulfate (29 ml) and an aqueous solution of sodium hydroxide (10N, 80 ml) at a temperature below 30°C. After stirring at room temperature for 2 hours, the reaction solution was diluted with water and extracted with benzene. After washing the benzene layer with water, the solvent was removed under reduced pressure and the oily residue was purified by column chromatography on silica gel (100–120 mesh) using a tetrahydrofuran/benzene (1:3) mixture as an eluent. The obtained crystals were recrystallized from ethanol to obtain 18.3 g of N'-m-(m-methoxyphenoxymethyl)phenyl-N-methoxy-N-methylurea (Compound No. 20) as white crystals. M.P., 76–79.5°C.

Elementaly analysis: Calcd. for $C_{17}H_{20}N_2O_4$: C, 64.53 %; H, 6.38 %;N, 8.86 %. Found: C, 64.60 %; H, 6.45 %; N, 8.74 %.

NMRδCDCl$_3$: 3.13 (s, 3H), 3.71 (s, 6H), 4.95 (s, 2H), 6.46–7.50 (8H), 7.58 (s, 1H).

Example 3 (Procedure (C))

To a solution of 3,4-dichlorophenol (16.3 g) in ethanol (100 ml) was added 50 % aqueous potassium hydroxide solution (12.3 g). To the mixture, a solution of N'-m-chloromethylphenyl-N,N-dimethylurea (21.3 g) in ethanol (50 ml) was added dropwise at 70 to 80°C. Thereafter, the reaction mixture was heated under reflux for 2 hours and allowed to stand at room temperature. The mixture was diluted with water and extracted with benzene. After washing the benzene layer with water, the solvent was removed under reduced pressure. The residue was recrystallized from ethanol to obtain 27.3 g of N'-m-(3,4-dichlorophenoxymethyl)phenyl-N,N-dimethylurea (Compound No. 29) as white crystals. M.P., 143–145°C.

Elementary analysis: Calcd. for $C_{16}H_{16}O_2N_2Cl_2$: C, 56.65 %; H, 4.76 %; N, 8.26 %; Cl, 20.90 %. Found: C, 56.46 %; H, 4.90 %; N, 8.41%; Cl, 20.77 %.

NMRδCDCl$_3$: 2.94 (s, 6H), 4.93 (s, 2H), 6.60–7.60 (7H), 7.92 (s, 1H).

Example 4 (Procedure (A))

Dried dimethylamine was bubbled into a solution of 4-(3-methylphenoxymethyl)phenyl isocyanate (11.3 g) in benzene (50 ml) at a temperature below 30°C for 10 minutes. After stirring at room temperature for 1 hour, the solvent was removed under reduced pressure, and the residue was recrystallized from ethanol to obtain 5.5 g of N'-4-(3-methylphenoxymethyl)phenyl-N,N-dimethylurea (Compound No. 46) as white needles. M.P., 135–136°C.

Elementary analysis: Calcd. for $C_{17}H_{20}O_2N_2$: C, 71.67 %; H, 7.08 %; N, 9.85 %. Found: C, 71.65 %; H, 7.08 %; N, 9.85 %.

NMRδCDCl$_3$: 2.25 (s, 3H), 2.90 (s, 6H), 4.85 (s, 2H), 6.30 (broad s, 1H), 7.25–6.40 (8H).

Example 5 (Procedure (B))

To a mixture of N'-4-(3-methoxyphenoxymethyl)phenyl-N-hydroxyurea (5.76 g, 0.02 mole) and dimethyl sulfate (5.54 g, 0.044 mole) in toluene (60 ml) was added tetra-n-butylammonium bromide (0.065 g, 0.0002 mole). To the mixture, an aqueous solution of sodium hydroxide (10N, 4.4 ml, 0.044 mole) was added dropwise at 20 to 22°C over period of 30 minutes while stirring. After stirring at 20 to 22°C for 3 hours, an organic layer was washed with water, dried over sodium sulfate and concentrated. The residue was dried in vacuo to obtain 5.74 g of white crystal which was identified by elementary analysis and NMR spectra as N'-4-(3-methoxyphenoxymethyl)phenyl-N-methyl-N-methoxyurea (Compound No. 45). M.P., 76–79°C.

Elementary analysis: Calcd. for $C_{17}H_{20}O_4N_2$: C, 64.54 %; H, 6.37 %; N, 8.86 %. Found: C, 64.39 %; H, 6.32 %; N, 8.81 %.

NMRδCDCl$_3$: 3.00 (s, 3H), 3.58 (s, 3H), 3.60 (s, 3H), 4.78 (s, 2H), 6.00–7.40 (8H), 7.54 (1H).

Example 6 (Procedure (C))

To a solution of phenol (9.4 g) in ethanol (100 ml) was added 50 % aqueous potassium hydroxide solution (12.3 g). To the mixture, a solution of N'-4-chloromethylphenyl-N,N-dimethylurea (21.3 g) in ethanol (50 ml) was added dropwise at 70 to 80°C. Thereafter, the reaction mixture was heated under reflux for 2 hours and allowed to stand at room temperature. The mixture was diluted with water and extracted with benzene. After washing the benzene layer with water, the solvent was removed. The residue was recrystallized from ethanol to obtain 8.8 g of N'-4-(phenoxymethyl)phenyl-N,N-dimethylurea (Compound No. 70) as white needles. M.P., 138–139°C.

Elementary analysis: Calcd. for $C_{16}H_{18}O_2N_2$: C, 70.95 %; H, 6.69 %; N, 10.35 %. Found: C, 70.94 %; H, 6.69 %; N, 10.38 %.

NMRδCDCl$_3$: 2.92 (s, 6H), 4.90 (s, 2H), 6.70–8.00 (10H).

Example 7 (Procedure (D))

To a solution of 3-chlorophenyl-4-aminobenzyl ether (8.2 g) in dry pyridine (25 ml) was added dropwise dimethylcarbamoyl chloride (3.8 g) at 25 to 50°C while stirring. After stirring overnight, the reaction mixture was poured into ice water. After the mixture was allowed to stand for 2 hours, the organic layer was separated from the aqueous layer. The aqueous layer was extracted with chloroform and the extract was combined with the organic layer. The combined organic layer was washed with water, and the solvent was removed under reduced pressure. The residue was recrystallized from ethanol to obtain 4.1 g of N′-4-(3-chlorophenoxymethyl)phenyl-N,N-dimethylurea (Compound No. 42) as white crystals. M.P., 109–110°C.

Elementary analysis: Calcd. for $C_{16}H_{17}O_2N_2Cl$: C, 62.95 %; H, 5.61 %; N, 9.18 %; Cl, 11.61 %. Found: C, 62.92 %; H, 5.60 %; N, 9.19 %; Cl, 11.63 %.

NMR$\delta$$CDCl_3$: 2.90 (s, 6H), 4.80 (s, 2H), 6.20–7.20 (9H).

Example 8 (Procedure (A))

To a solution of p-(o-methoxyphenoxymethyl)phenyl isocyanate (22.5 g) in benzene (100 ml) was added dropwise at a temperature below 30°C a solution of monomethylamine (37.3 g) in benzene (100 ml). After the reaction mixture was allowed to stand at room temperature for 1 hour, the solvent was removed under reduced pressure. The residue was recrystallized from ethanol to obtain 17.3 g of N′-m-(o-methoxyphenoxymethyl)phenyl-N-methylurea (Compound No. 74) as white needles. M.P., 167–168°C.

Elementary analysis: Calcd. for $C_{17}H_{20}N_2O_4$: C, 64.53 %; H, 6.38 %; N, 8.86 %. Found: C, 64.57 %; H, 6.34 %; N, 8.89 %.

NMR$\delta$$CDCl_3$–$DMSOd_6$: 2.75 (d, 3H), 3.82 (s, 3H), 5.00 (s, 2H), 5.81 (m, 1H), 6.91 (s, 4H), 7.36 (m, 4H), 8.22 (s, 1H).

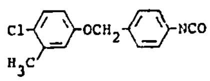
Example 9 (Preparation of the phenyl isocyanate (II))

A solution of 4-phenoxymethylaniline (10 g) in toluene (100 ml) was added dropwise to a solution of phosgene (20 g) in toluene (100 ml) at 10 to 20°C. The mixture was gradually heated and refluxed for 30 minutes. Thereafter, the reaction mixture was cooled to room temperature, and the solvent was evaporated under reduced pressure to give 7 g of 4-phenoxymethylphenyl isocyanate. M.P., 56–57°C.

Elementary analysis: Calcd. for $C_{14}H_{11}NO_2$: C, 74.64 %; H, 4.93 %; N, 6.22 %. Found: C, 74.53 %; H, 4.86 %; N, 6.35 %.

NMR$\delta$$CDCl_3$: 4.92 (s, 2H), 6.80–7.50 (9H).

In the same manner as above, the following phenyl isocyanate was obtained:



Melting point, 46 - 47°C

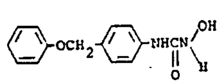
Example 10 (Preparation of the hydroxyurea (III))

An aqueous solution of sodium hydroxide (10N, 9.7 ml) was added dropwise to a solution of hydroxylamine hydrochloride (6.7 g) in water (10 ml) while cooling with ice. To the mixture, a solution of 4-(3-methyl-4-chlorophenoxymethyl)phenyl isocyanate (4.6 g) in toluene (50 ml) was slowly added at a temperature below 10°C. The reaction mixture was allowed to stand overnight at room temperature. The mixture was then extracted with ethyl acetate, and the ethyl acetate layer was washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure to obtain 4.1 g of N′-4-(3-methyl-4-chlorophenoxymethyl)phenyl-N-hydroxyurea. M.P., 155–156°C.

Elementary analysis: Calcd. for $C_{15}H_{15}O_3N_2Cl$: C, 58.72 %; H, 4.94 %; N, 9.13 %; Cl, 11.56 %. Found: C, 58.69 %; H, 4.85 %; N, 9.01 %; Cl, 11.55 %.

NMR$\delta$$CDCl_3$: 2.30 (s, 3H), 5.00 (s, 2H), 6.70–7.80 (7H), 8.75 (s, 1H), 8.80 (s, 1H), 8.90 (s, 1H).

In the same manner as above, the following hydroxyurea was obtained:



Melting point, 158 - 159°C

In the practical usage of the compounds (I), they may be applied without additions or in any preperation form such as wettable powders, emulsifiable concentrates, water dispersible liquids, granules, fine granules or dusts.

In producing such preparation form, a solid or liquid carrier or diluent may be used. As for the solid carrier or diluent, there may be given mineral powders (e.g. kaolin, bentonite, clay, montmorillonite, talc, diatomaceous earth, mica, vermiculite, gypsum, calcium carbonate, apatite), vegetable powders (e.g. soybean powder, wheat flour, wooden powder, tobacco

powder, starch, crystalline cellulose), high molecular weight compounds (e.g. petroleum resin), alumina, wax and the like.

Examples of liquid carriers and diluents, are alcohols (e.g. methyl alcohol, ethyl alcohol, ethylene glycol, benzyl alcohol), aromatic hydrocarbons (e.g. toluene, benzene, xylene, methylnaphthlene), halogenated hydrocarbons (e.g. chloroform, carbon tetrachloride, monochlorobenzene), ethers (e.g. dioxane, tetrahydrofuran), ketones (e.g. acetone, methyl ethyl ketone, cyclohexanone), esters (e.g. ethyl acetate, butyl acetate, ethylene glycol acetate), acid amides (e.g. dimethylformamide), nitriles (e.g. acetonitrile) and water.

A surface active agent may be used to assist emulsification, dispersion or spreading. Any of the non-ionic, anionic, cationic and amphoteric type of agents may be used. Examples of the surface active agent include polyoxyethylene alkyl ether, polyoxyethylene alkylaryl ethers, polyoxyethylene fatty acid esters, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, oxyethylene polymers, oxypropylene polymers, polyoxyethylene alkyl phosphates, fatty acid salts, alkyl sulfates, alkyl sulfonates, alkylaryl sulfonates, alkyl phosphates, quaternary ammonium salts and the like. The surface active agent is not of course limited to these compounds. If necessary, gelatin, casein, sodium alginate, starch, agar, polyvinyl alcohol or the like may be used as an auxiliary agent.

In the herbicidal and/or fungicidal composition of the invention, the content of the compound (I) as an active ingredient may be from 1 to 100 % by weight, preferably from 5 to 80 % by weight.

Practical embodiments of the herbicidal and/or fungicidal composition according to the invention are illustratively shown in the following examples wherein parts and % are by weight.

Preparation Example 1

Eighty parts of Compound No. 4, 5 parts of polyoxyethylene alkylaryl ether and 15 parts of synthetic silicon oxide hydrate are well mixed while being powdered to obtain a wettable powder.

Preparation Example 2

Thirty parts of Compound No. 10, 7 parts of polyoxyethlene alkylaryl ether, 3 parts of alkylaryl sulfonate and 60 parts of xylene are well mixed to obtain an emulsifiable concentrate.

Preparation Example 3

One part of Compound No. 20, 1 part of white carbon, 5 parts of ligninsulfonate and 93 parts of clay are well mixed while being powdered. The mixture is then well kneaded with water, granulated and dried to obtain a granule.

Preparation Example 4

Fourty parts of bentonite, 5 parts of ligninsulfonate and 55 parts of clay are well mixed while being powdered. The mixture is then well kneaded with water, granulated and dried to obtain a granule containing no active ingredient. The granule is then impregnated with 5 parts of Compound No. 8 to obtain a granule.

Preparation Example 5

Three parts of Compound No. 30, 0.5 part of isopropyl phosphate, 66.5 parts of clay and 30 parts of talc are well mixed while being powdered to obtain a dust.

Preparation Example 6

Two parts of Compound No. 58, 88 parts of clay and 10 parts of talc are well mixed while being powdered to obtain a dust containing 2 % of the active ingredient.

Preparation Example 7

Three parts of Compound No. 82, 67 parts of clay and 30 parts of talc are well mixed while being powdered to obtain a dust containing 3 % of the active ingredient.

The compounds (I) of the invention may be used together with other herbicides to improve their activity as herbicides, and in some cases, a synergistic effect can be expected. As the other herbicides, there may be exemplified phenoxy series herbicides such as 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenoxybutyric acid (including esters and salts thereof); diphenyl ether series herbicides such as 2,4-dichlorophenyl-4′-nitrophenyl ether, 2,4-dichlorophenyl-4′-nitro-3′-methoxyphenyl ether, 2,4-dichlorophenyl-3′-methoxycarbonyl-4′-nitrophenyl ether and 2-chloro-4-trifluoromethylphenyl-3′-hydroxycarbonyl-4′-nitrophenyl ether; triazine series herbicides such as 2-chloro-4,6-bisethylamino-1,3,5-triazine, 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine and 2-methylthio-4,6-bisethylamino-1,3,5-triazine; urea series herbicides such as 3-(3-,4-dichlorophenyl)-1,1-dimethylurea, 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea, 3-[4-(4-chlorophenoxy)phenyl]-1,1-dimethylurea and 3-(α,α,α-trifluoro-m-tolyl)-1,1-dimethylurea; car-

bamate series herbicides such as isopropyl-N-(3-chlorophenyl)carbamate, methyl-N-(3,4-dichlorophenyl)carbamate and 4-chloro-2-butynyl-m-chlorocarbanilate; thiolcarbamate series herbicides such as S-(4-chlorobenzyl)-N,N-diethylthiolcarbamate and S-ethyl dipropylthiolcarbamate; acid anilide series herbicides such as 3,4-dichloropropionanilide, N-methoxymethyl-2,6-diethyl-2-chloroacetanilide and 2-chloro-2′,6′-diethyl-N-(butoxymethyl)acetanilide; uracil series herbicides such as 5-bromo-3-sec-butyl-6-methyluracil and 3-cyclohexyl-5,6-trimethyleneuracil; pyridinium salt series herbicides such as 1,1′-dimethyl-4,4′-bispyridinium dichloride; organic phosphorus series herbicides such as N-(phosphonomethyl)glycine, O-methyl-O-(2-nitro-4-methylphenyl)-N-isopropylphosphoroamidothioate and O-ethyl-O-(2-nitro-5-methylphenyl)-N-sec-butylphosphoroamidothioate; toluidine series herbicides such as α,α,α,-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine; N-sec-butyl-4-tert-butyl-2,6-dinitroaniline; 3,5-dinitro-N^4, N^4-dipropylsulfanylamide; 5-tert-butyl-3-(2,4-dichloro-5-isopropoxyphenyl)-1,3,4-oxadiazolin-2-one; 3-isopropyl-1H-2,1,3-benzothiadiazine(4)-3H-one-2,2-dioxide (including salts thereof); 2-(β-naphthoxy)-propionanilide; 2-(α-naphthoxy)-N,N-diethylpropionanilide; 3-amino-2,5-dichlorobenzoic acid; 2-sec-butyl-4,6-dinitrophenol; N-1-naphthylphthalamic acid; 2-[1-(N-allyloxyamino)-butylidene-5,5-dimethyl-4-methoxycarbonyl-cyclohexane-1,3-dione (including salts thereof); 2-[4-(3,5-dichloropyridine-2-hydroxy)-phenoxy]propionic acid (including salts thereof), and 2-[4-(2,4-dichlorophenoxy)phenoxy]propionic acid (including esters and salts thereof). The additional herbicides are not of course limited to these examples.

The compounds (I) may be also applied together with common fungicides, microbial insecticides, pyrethroid series insecticides, other insecticides, plant growth regulators or fertilizers.

Examples of the fungicides which may be used in combination with the compounds (I) are as follows: N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide, S-n-butyl-S-p-t-butylbenzyl-N-3-pyridyldithiocarbonimidate, O,O-dimethyl-O-2,6-dichloro-4-methylphenyl phosphorothioate, methyl-N-benzimidazol-2-yl-N-(butylcarbamoyl)carbamate, N-trichloromethylthio-4-cyclohexene-1,2-dicarboximide, cis-N-(1,1,2,2-tetrachloroethylthio)-4-cyclohexene-1,2-dicarbox-imide, polyoxin, streptomycin, zinc ethylenebisdithiocarbamate, zinc dimethylthiocarbamate, manganese ethylenebisdithiocarbamate, bis(dimethylthiocarbamoyl) disulfide, tetrachloroisophthalonitrile, 8-hydroxyquinoline, dodecylguanidine acetate, 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide, N′-dichlorofluoromethylthio-N,N-dimethyl-N′-phenylsulfamide, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-2-butanone, 1,2-bis(3-methoxycarbonyl-2-thioureido)benzene, etc. Examples of the insecticides which may be employed together with the compounds (I) of the invention are O,O-dimethyl-O-(4-nitro-m-tolyl)phosphorothioate, O-p-cyanophenol-O,O-dimethylphosphorothioate, O-p-cyanophenyl-O-ethylphenylphosphonothioate, O,O-dimethyl-S-(N-methylcarbamoylmethyl)phosphorodithioate, 2-methoxy-4H-1,3,2-benzodioxaphosphorin-2-sulfide, O,O-dimethyl-S-(1-ethoxycarbonyl-1-phenylmethyl)phosphorodithioate, 1-cyano-3-phenoxybenzyl-2-(4-chlorophenyl)-isovaleate, 3-phenoxybenzyl-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate, and 3-phenoxybenzylchrysanthemate.

The dosage rate of the compounds (I) as herbicides depend upon their nature, the sort of cultivated plants, the application method, the weather, etc. Generally, however, the dosage rate is from 2 to 200 grams, preferably from 5 to 50 grams, of the active ingredient per are.

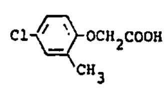
The dosage rate of the compounds (I) as fungicides also depend upon their preparation methods, kinds of diseases, sorts of cultivated plants, time of application, etc. In general, the active ingredient may be applied in an amount of from 0.2 to 50 grams per are, and the concentration thereof is preferably from 0.001 to 1.0 % by weight.

The application of the compounds (I) as herbicides and/or fungicides will be illustrated in the following Examples wherein the phytotoxicity to cultivated plants and the herbicidal activity on weeds were evaluated as follows: the aereal parts of the test plants were cut off and weighed (fresh weight); the percentage of the fresh weight of the treated plant to that of the untreated plant was calculated with the latter fresh weight taken as 100; and the crop damage and the herbicidal activity were evaluated by the standard given in the table below. The rating values of phytotoxicity, 0 and 1, and those of herbicidal effect, 5 and 4, are generally regarded as satisfactory to protect cultivated plants and to control weeds, respectively. The rating values in the paddy rice test alone were calculated from the dry weight of plant.

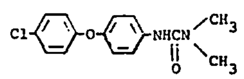
Rating value	Fresh weight (percentage to untreated plot) (%)	
	Cultivated plant	Weed
5	0–39	0
4	40–59	1–10
3	60–79	11–20
2	80–89	21–40
1	90–99	41–60
0	100	61–100

The following control compounds were used in the Examples.

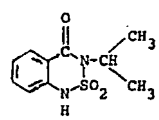
MCP:



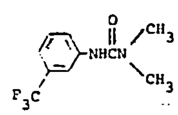
Chloroxuron:



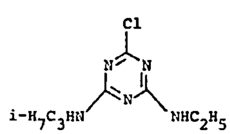
Bentazon:



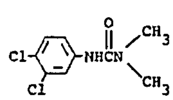
Fluometuron:



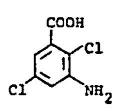
Atrazine:



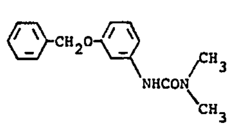
Diuron:



Chloramben:



N'-(m-Benzyloxyphenyl)-N,N-dimethylurea (U.S. Patent 3,819,697):



Example 11 (Paddy rice test)

Wagner's pots (1/5000 are) were each filled with 1.5 kg of paddy field soil containing the seeds of weeds and kept under flooded conditions. The seedlings of rice plant at a 3-leaf stage were transplanted thereto, and after the seeds of barnyard grass were sowed therein, the seedlings were grown for 15 days in a green-house. Thereafter, the required amount of the wettable powder of each test compound was diluted with water and applied to the soil under flooded conditions. Twenty-five days after the application, the evaluation of herbicidal activity and phytotoxicity was made on the rice plants and barnyard grass as well as broad-leaved weeds (e.g. pickerel weed (*Monochoria vagianalis*), false pimpernel (*Linderna pyxidaria*), toothcup (*Rotala indica*) Koehne)) and nutsedge sp. (*Cyperus difformis*). The results are shown in Table 1.

Table 1

Compound No.	Dosage (weight of active ingredient, g/are)	Evaluation of crop damage and herbicidal activity			
		Rice plant	Barn-yard grass	Broad-leaved weed	Nutsedge sp.
1	20	0	4	5	5
	10	0	4	5	5
2	20	0	4	5	5
	10	0	4	5	5
3	20	0	4	5	5
	10	0	4	5	5
4	20	0	5	5	5
	10	0	5	5	5
5	20	0	5	5	5
	10	0	4	5	5
6	20	0	5	5	5
	10	0	5	5	5
7	20	0	5	5	5
	10	0	5	5	5
8	20	0	5	5	5
	10	0	5	5	5
9	20	0	5	5	5
	10	0	5	5	5
10	20	0	5	5	5
	10	0	5	5	5
11	20	0	4	5	5
	10	0	4	5	5
12	20	0	4	5	5
	10	0	4	5	5
13	20	0	4	5	5
	10	0	4	5	5
14	20	0	4	5	5
	10	0	4	5	5
15	20	0	5	5	5
	10	0	4	5	5
16	20	0	4	5	5
	10	0	4	5	5
17	20	0	4	5	5
	10	0	4	5	5
18	20	0	5	5	5
	10	0	4	5	5
19	20	0	4	5	5
	10	0	4	5	5
20	20	0	4	5	5
	10	0	4	5	5
21	40	0	4	5	5
	20	0	4	5	5
22	20	0	4	5	5
	10	0	4	5	5
23	40	0	4	5	5
	20	0	4	5	5
24	20	0	5	5	5
	10	0	4	5	5
26	20	0	4	5	5
	10	0	4	5	5
27	20	0	4	5	5
	10	0	4	5	5
28	20	0	4	5	5
	10	0	4	5	5
29	20	0	5	5	5
	10	0	3	5	5

Table 1 continued

Compound No.	Dosage (weight of active ingredient, g/are)	Evaluation of crop damage and herbicidal activity			
		Rice plant	Barn-yard grass	Broad-leaved weed	Nutsedge sp.
30	20	0	4	5	5
	10	0	4	5	5
31	40	0	4	5	5
	20	0	4	5	5
32	20	0	5	5	5
	10	0	5	5	5
33	20	0	4	5	5
	10	0	4	5	5
34	20	0	4	5	5
	10	0	4	5	5
35	20	0	5	5	5
	10	0	5	5	5
36	20	0	4	5	5
	10	0	4	5	5
37	20	0	4	5	5
	10	0	4	5	5
39	20	0	4	5	5
	10	0	4	5	5
40	20	0	4	5	5
	10	0	4	5	5
41	20	0	5	5	5
	10	0	4	5	5
42	20	0	4	5	5
	10	0	4	5	5
43	20	0	5	5	5
	10	0	5	5	5
44	20	0	4	5	5
	10	0	4	5	5
45	20	0	4	5	5
	10	0	4	5	5
46	20	0	5	5	5
	10	0	4	5	5
47	20	0	5	5	5
	10	0	4	5	5
48	20	0	5	5	5
	10	0	5	5	5
49	20	0	5	5	5
	10	0	4	5	5
50	20	0	5	5	5
	10	0	5	5	5
51	20	0	5	5	5
	10	0	5	5	5
52	20	0	4	5	5
	10	0	4	5	5
53	40	0	4	5	5
	20	0	4	5	5
54	20	0	5	5	5
	10	0	5	5	5
57	40	0	4	5	5
	20	0	4	5	5
58	20	0	5	5	5
	10	0	4	5	5
59	20	0	5	5	5
	10	0	4	5	5
60	20	0	5	5	5
	10	0	5	5	5

Table 1 continued

Compound No.	Dosage (weight of active ingredient, g/are)	Evaluation of crop damage and herbicidal activity			
		Rice plant	Barn-yard grass	Broad-leaved weed	Nutsedge sp.
61	20	0	5	5	5
	10	0	4	5	5
62	20	0	5	5	5
	10	0	5	5	5
63	20	0	5	5	5
	10	0	5	5	5
64	20	0	4	5	5
	10	0	4	5	5
65	20	0	5	5	5
	10	0	5	5	5
66	20	0	5	5	5
	10	0	4	5	5
67	20	0	5	5	5
	10	0	4	5	5
69	20	0	4	5	5
	10	0	4	5	5
70	20	0	4	5	5
	10	0	4	5	5
73	40	0	4	5	5
	20	0	4	5	5
74	40	0	4	5	5
	20	0	4	5	5
75	20	0	5	5	5
	10	0	4	5	5
78	40	0	4	5	5
	20	0	4	5	4
79	20	0	4	5	5
	10	0	4	5	5
80	20	0	5	5	5
	10	0	4	5	5
81	20	0	5	5	5
	10	0	4	5	5
82	20	0	5	5	5
	10	0	4	5	5
83	20	0	4	5	5
	10	0	4	5	5
84	20	0	5	5	5
	10	0	4	5	5
MCP	20	3	4	5	5
	10	2	3	5	5
N'-(m-Benzyl-oxyphenyl)-N,N-dimethyl-urea	20	1	2	5	4
	10	0	2	5	4

Example 12 (Post-emergence application test (weeds))

Plastic trays (35 cm × 25 cm × 10 cm (high)) were filled with upland field soil, and the seeds of redroot pigweed, common lambsquarters, radish, sunflower, cocklebur, annual morningglory, black nightshade, large crabgrass, barnyard grass and green foxtail were separately sowed in the trays and grown for 3 weeks in a green-house. The required amount of the test compound was sprayed on the foliage of the test plants over the top by means of a small hand sprayer. After the spraying, the test plants were grown for further 3 weeks in the green-house, and herbicidal activity was examined. The results are shown in Table 2. In the above foliar

application, the test compounds were each formulated into an emulsifiable concentrate, and the required amount of the emulsifiable concentrate was dispersed in water for application at a spray volume of 5 liters per are and applied with the addition of a wetting agent. At the time of application, the weeds were in a 2- to 4-leaf stage and 2 to 12 cm in height although there was some difference depending upon the kind of weed.

Table 2

Compound No.	Dosage (weight of active ingredient, g/are)	Herbicidal activity									
		Redroot pigweed	Common lambs-quarters	Radish	Sunflower	Cock-lebur	Annual morning-glory	Black night-shade	Large crab-grass	Barn-yard grass	Green fox-tail
1	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	4	4
2	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	5	4
3	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	4	4
4	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	5	5
5	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	4	5
6	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	5	5
7	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	5	5
8	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	5	5
9	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	4	5
10	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	4	5
11	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	4	4
13	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	4	4	4
14	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	4	4
15	20	5	5	5	5	5	5	5	5	4	5
	10	5	5	5	5	5	5	5	4	4	4
16	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	4	4	4
17	20	5	5	5	5	5	5	5	5	5	4
	10	5	5	5	5	5	5	5	4	4	4
18	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	5	4
20	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	4	4

Table 2 continued

Compound No.	Dosage (weight of active ingredient, g/are)	Herbicidal activity									
		Redroot pigweed	Common lambs-quarters	Radish	Sunflower	Cock-lebur	Annual morning-glory	Black night-shade	Large crab-grass	Barn-yard grass	Green fox-tail
22	20	5	5	5	5	5	5	5	4	5	4
	10	5	5	5	5	5	5	5	4	4	4
24	20	5	5	5	5	5	5	5	5	5	4
	10	5	5	5	5	5	5	5	4	5	4
26	20	5	5	5	5	5	5	5	4	4	5
	10	5	5	5	5	5	5	5	4	4	4
27	20	5	5	5	5	5	5	5	4	5	4
	10	5	5	5	5	5	5	5	4	4	4
28	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	4	4	4
29	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	4	4
30	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	4	4
32	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	5	5
33	20	5	5	5	5	5	5	5	5	4	4
	10	5	5	5	5	5	5	5	4	4	4
34	20	5	5	5	5	5	5	5	5	5	4
	10	5	5	5	5	5	5	5	4	5	4
35	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	4	5
36	20	5	5	5	5	5	5	5	5	4	4
	10	5	5	5	5	5	5	5	4	4	4
37	20	5	5	5	5	5	5	5	5	5	4
	10	5	5	5	5	5	5	5	4	4	4
39	20	5	5	5	5	5	5	5	5	4	4
	10	5	5	5	5	5	5	5	4	4	4
40	20	5	5	5	5	5	5	5	5	5	4
	10	5	5	5	5	5	5	5	4	4	4
42	20	5	5	5	5	5	5	5	4	4	5
	10	5	5	5	5	5	5	5	4	3	3
43	20	5	5	5	5	5	5	4	4	4	5
	10	5	5	5	5	5	5	4	3	4	4
44	40	5	5	5	5	5	5	5	5	4	4
	20	5	5	5	5	5	5	5	3	3	4

Table 2 continued

Compound No.	Dosage (weight of active ingredient, g/are)	Herbicidal activity									
		Redroot pigweed	Common lambs-quarters	Radish	Sunflower	Cock-lebur	Annual morning-glory	Black night-shade	Large crab-grass	Barn-yard grass	Green fox-tail
46	20	5	5	5	5	5	5	5	4	4	5
	10	5	5	5	5	5	5	5	3	4	3
47	20	5	5	5	5	5	5	4	4	4	4
	10	5	5	5	5	5	5	4	3	4	4
48	20	5	5	5	5	5	5	5	5	4	5
	10	5	5	5	5	5	5	5	3	4	4
50	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	5	5	5
51	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	4	5
52	40	5	5	5	5	5	5	5	4	5	5
	20	5	5	5	5	5	5	5	4	3	3
56	20	5	5	5	5	5	5	5	4	4	4
	10	5	5	5	5	5	5	5	3	4	3
57	20	5	5	5	5	5	5	5	4	4	5
	10	5	5	5	5	5	4	4	3	3	3
58	20	5	5	5	5	5	5	5	5	4	5
	10	5	5	5	5	5	5	5	3	4	4
59	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	4	3	3
60	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	5	5
61	20	5	5	5	5	5	5	5	5	4	4
	10	5	5	5	5	5	5	5	3	4	3
62	20	5	5	5	5	5	5	5	4	5	4
	10	5	5	5	5	5	5	5	4	3	4
63	20	5	5	5	5	5	5	5	4	4	5
	10	5	5	5	5	5	5	5	4	3	4
64	20	5	5	5	5	5	5	5	4	4	5
	10	5	5	5	5	5	5	5	3	3	3
65	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	3	4	4
66	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	4	3
67	20	5	5	5	5	5	5	5	4	4	4
	10	5	5	5	5	5	5	5	4	4	3

Table 2 continued

Compound No.	Dosage (weight of active ingredient, g/are)	Herbicidal activity: Redroot pigweed	Common lambs-quarters	Radish	Sunflower	Cock-lebur	Annual morning-glory	Black night-shade	Large crab-grass	Barn-yard grass	Green fox-tail
68	40	5	5	5	5	5	5	5	4	4	4
	20	5	5	5	5	5	5	5	3	3	4
70	20	5	5	5	5	5	5	5	5	4	5
	10	5	5	5	5	5	5	5	3	4	3
71	40	5	5	5	5	5	5	5	4	4	5
	20	5	5	5	5	5	5	5	3	3	5
75	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	4	3	3
76	40	5	5	5	5	5	5	5	5	4	5
	20	5	5	5	5	5	5	5	3	3	3
77	40	5	5	5	5	5	5	5	4	5	4
	20	5	5	5	5	5	5	5	3	3	4
79	20	5	5	5	5	5	5	5	4	4	5
	10	5	5	5	5	5	5	5	3	4	3
80	20	5	5	5	5	5	5	5	4	4	4
	10	5	5	5	5	5	5	5	4	3	4
81	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	4	5
82	20	5	5	5	5	5	5	5	4	5	5
	10	5	5	5	5	5	5	5	4	4	4
83	20	5	5	5	5	5	5	5	5	4	4
	10	5	5	5	5	5	5	5	3	3	4
84	20	5	5	5	5	5	5	5	5	5	5
	10	5	5	5	5	5	5	5	4	4	3
Chloro-xuron	20	5	5	5	5	5	5	5	4	3	4
	10	5	5	5	5	5	5	5	2	3	3
Bentazon	20	3	5	5	5	5	4	5	1	2	0
	10	2	5	5	5	5	2	4	0	1	0
N'-(m-Benzyl-oxyphenyl)-N,N-dimethyl-urea	20	4	5	4	5	4	3	5	3	2	3
	10	4	5	4	5	3	1	4	1	2	2

Example 13 (Post-emergence application test (cultivated plants))

Wagner's pots (1/5000 are) were each filled with upland field soil, and the seeds of soybean, cotton, sugar beet, corn, wheat and rice plant were sowed in the pots and grown for 3 weeks in a green-house. The required amount of the test compound was sprayed to the foliage of the test plants over the top by means of a small hand sprayer. After the spraying, the test plants were grown for further 3 weeks in the green-house, and phytotoxicity was examined. The results are shown in Table 3. In the above foliar application, the test compounds were each formulated into an emulsifiable concentrate, and the required amount of the emulsifiable concentrate was dispersed in water for application at a spray volume of 5 liters per are and applied with the addition of a wetting agent. At the time of application, soybean was in the second trifoliate stage, cotton in the 1-leaf stage, sugar beet in the 2-leaf stage, corn in the 2-leaf stage, wheat in the 2-leaf stage and rice plant in the 2-leaf stage.

Table 3

Compound No.	Dosage (weight of active ingredient g/are)	Phytotoxicity					
		Soybean	Cotton	Sugar Beet	Corn	Wheat	Rice plant
1	20	1	–	–	1	1	–
	10	0	–	–	1	0	–
2	20	1	–	–	–	1	–
	10	0	–	–	–	1	–
3	20	–	1	–	–	–	1
	10	–	0	–	–	–	0
5	20	1	–	–	–	–	1
	10	1	–	–	–	–	1
10	20	–	–	–	–	1	1
	10	–	–	–	–	0	0
13	20	1	–	–	–	0	1
	10	1	–	–	–	0	0
16	20	1	–	1	–	1	–
	10	1	–	1	–	0	–
17	20	0	0	–	1	1	0
	10	0	0	–	1	0	0
18	20	–	1	–	1	–	0
	10	–	0	–	1	–	0
20	20	0	–	–	1	–	1
	10	0	–	–	0	–	0
24	20	0	1	–	–	–	–
	10	0	0	–	–	–	–
28	20	1	0	–	–	–	0
	10	0	0	–	–	–	0
29	20	–	1	–	–	1	0
	10	–	1	–	–	1	0
33	20	1	–	–	1	1	1
	10	1	–	–	1	1	0
35	20	1	–	–	–	1	–
	10	0	–	–	–	0	–
36	20	1	1	–	–	0	–
	10	0	0	–	–	0	–
40	20	1	1	–	–	–	0
	10	0	1	–	–	–	0
43	20	0	–	–	1	–	0
	10	0	–	–	1	–	0
48	20	–	–	0	–	0	–
	10	–	–	0	–	0	–
50	20	1	1	–	–	0	–
	10	0	0	–	–	0	–
58	20	–	–	1	–	–	0
	10	–	–	1	–	–	0
60	20	–	–	–	1	–	–
	10	–	–	–	0	–	–

Table 3 continued

Compound No.	Dosage (weight of active ingredient g/are)	Phytotoxicity Soybean	Cotton	Sugar Beet	Corn	Wheat	Rice plant
61	20	–	1	–	1	–	–
	10	–	0	–	0	–	–
67	20	1	–	–	–	–	0
	10	0	–	–	–	–	0
70	20	–	–	1	–	–	–
	10	–	–	0	–	–	–
75	20	0	–	–	–	–	0
	10	0	–	–	–	–	0
79	20	–	0	–	–	0	–
	10	–	0	–	–	0	–
81	20	0	1	–	–	0	–
	10	0	0	–	–	0	–
82	20	–	–	–	–	–	0
	10	–	–	–	–	–	0
84	20	0	–	–	–	–	–
	10	0	–	–	–	–	–
Chloro-xuron	20	2	–	–	–	–	–
	10	1	–	–	–	–	–
Bentazon	20	0	–	–	1	–	0
	10	0	–	–	0	–	0
Fluo-meturon	20	–	2	–	–	–	–
	10	–	1	–	–	–	–
Atrazine	20	–	–	–	1	–	–
	10	–	–	–	1	–	–
Diuron	20	5	5	5	5	5	–
	10	5	5	5	4	5	–

Example 14 (Pre-emergence application test)

Plastic trays (35 cm × 25 cm × 10 cm (high)) were filled with upland field soil, and the seeds of soybean, cotton, sugar beet, corn, wheat, rice plant, redroot pigweed, common lambsquarters, radish, common purslane and large crabgrass were sown. The required amount of an emulsifiable concentrate was dispersed in water and sprayed at a volume of 5 liters per are to the whole surface of the soil by means of a small hand sprayer. After the spraying, the trays were placed in a green-house for 20 days, and phytotoxicity and herbicidal activity were examined. The results are shown in Table 4.

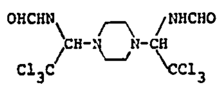
Table 4

Compound No.	Dosage (weight of active ingredient, g/are)	Phytoxicity: Soybean	Cotton	Sugar beet	Corn	Wheat	Rice plant	Herbicidal activity: Redwood pigweed	Common lambs-quarters	Radish	Common purslane	Large crab grass
2	40	0	0	0	0	0	0	5	5	5	5	5
	20	0	0	0	0	0	0	5	5	5	5	4
4	40	0	0	0	0	0	0	5	5	5	5	5
	20	0	0	0	0	0	0	5	5	5	5	5
6	40	0	0	0	0	0	0	5	5	5	5	5
	20	0	0	0	0	0	0	5	5	5	5	5
9	40	0	0	0	0	0	0	5	5	5	5	5
	20	0	0	0	0	0	0	5	5	5	5	4
18	40	0	0	0	0	0	0	5	5	5	5	4
	20	0	0	0	0	0	0	5	5	5	5	4
20	40	0	0	0	0	0	0	5	5	5	5	4
	20	0	0	0	0	0	0	5	5	5	5	4
29	40	0	0	0	0	0	0	5	5	5	5	5
	20	0	0	0	0	0	0	5	5	5	5	5
32	40	0	0	0	0	0	0	5	5	5	5	5
	20	0	0	0	0	0	0	5	5	5	5	5
35	40	0	0	0	0	0	0	5	5	5	5	5
	20	0	0	0	0	0	0	5	5	5	5	4
42	80	0	0	0	0	0	0	5	5	5	5	4
	40	0	0	0	0	0	0	5	5	5	5	4
46	80	0	0	0	0	0	0	5	5	5	5	4
	40	0	0	0	0	0	0	5	5	5	5	4
48	40	0	0	0	0	0	0	5	5	5	5	5
	20	0	0	0	0	0	0	5	5	5	5	4
50	40	0	0	0	0	0	0	5	5	5	5	5
	20	0	0	0	0	0	0	5	5	5	5	5
52	80	0	0	0	0	0	0	5	5	5	5	4
	40	0	0	0	0	0	0	5	5	5	5	4
55	80	0	0	0	0	0	0	5	5	5	5	5
	40	0	0	0	0	0	0	5	5	5	5	4
61	40	0	0	0	0	0	0	5	5	5	5	5
	20	0	0	0	0	0	0	5	5	5	5	4
62	80	0	0	0	0	0	0	5	5	5	5	4
	40	0	0	0	0	0	0	5	5	5	5	4

Table 4 continued

Compound No.	Dosage (weight of active ingredient, g/are)	Phytoxicity						Herbicidal activity				
		Soybean	Cotton	Sugar beet	Corn	Wheat	Rice plant	Redwood pigweed	Common lambs-quarters	Radish	Common purslane	Large crab grass
72	80	0	0	0	0	0	0	5	5	5	5	5
	40	0	0	0	0	0	0	5	5	5	5	4
75	80	0	0	0	0	0	0	5	5	5	5	4
	40	0	0	0	0	0	0	5	5	5	5	4
80	40	0	0	0	0	0	0	5	5	5	5	5
	20	0	0	0	0	0	0	5	5	5	5	4
81	40	0	0	0	0	0	0	5	5	5	5	5
	20	0	0	0	0	0	0	5	5	5	5	4
Chlor-amben	20	0	4	–	3	1	–	2	2	0	5	3
	10	0	3	–	2	0	–	2	1	0	5	2
Diuron	20	5	3	–	4	5	–	5	5	5	5	4
	10	4	1	–	2	4	–	5	5	5	5	3

The application of the compounds (I) as fungicides will be illustrated in the following Example wherein a commercially available fungicide known under the generic name "triforine" and having the following formula was used for comparison:



Example 15 (Protective effect on leaf rust of wheat)

Plastic pots (150 ml volume) were filled with sandy soil, and 10 to 15 seeds of wheat (var.: Nohrin No. 51) were sown and grown up to the one-leaf stage in an air-controlled room kept at a temperature of 18 to 23°C for 7 days. The wheats were inoculated with *Puccinia recondita* and placed in a humid chamber for 16 hours. Then, each of the emulsifiable concentrates containing the test compounds was diluted with water and sprayed on the test plants at a rate of 15 ml/pot. The test plants were placed in a chamber kept at 23°C and grown under a fluorescent lamp for an additional 10 days. The degree of infection at the one-leaf stage was examined by the following method: the leaves examined were measured for a percentage of infected area and classified into the corresponding disease indices, 0, 0.5, 1, 2 and 4. The disease severity was calculated according to the following equation:

Disease index	Infection state
0	No infected surface area
0.5	Infected surface area of less than 5%
1	Infected surface area of less than 20 %
2	Infected surface area of less than 50 %
4	Infected surface area of more than 50 %

$$\text{Disease severity (\%)} = \frac{\Sigma(\text{Disease index}) \times (\text{Number of leaves})}{4 \times (\text{Total number of leaves examined})} \times 100$$

The prevention value was calculated according to the following equation:

$$\text{Prevention value (\%)} = 100 - \frac{\text{Disease severity in treated pots}}{\text{Disease severity in untreated pots}}$$

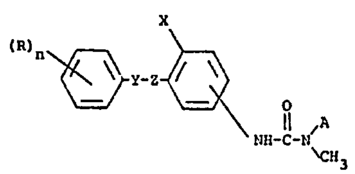
The results are shown in Table 5, from which it is understood that the compounds (I) of the present invention exhibit a pronounced protective effect against leaf rust of wheat.

Table 5

Compound No.	Concentration of active ingredient (ppm)	Prevention value (%)
1	500	100
2	500	100
5	500	100
16	500	100
23	500	90
28	500	95
39	500	100
42	500	100
43	500	100
50	500	99
Triforine	500	82

CLAIMS

1. A compound of the formula:



wherein A is a hydrogen atom, a methyl group or a methoxy group, the Rs are same as or different from each other and each is a halogen atom, a lower alkyl group, a lower alkoxy group, a lower alkylthio group a trifluoromethyl group, a cyano group or a methylenedioxy group, X is a hydrogen atom or a halogen atom, Y is an oxygen atom or a sulfur atom, Z is a lower alkylene group and n is an integer of 0 to 3, provided that the substituted ureido group is present at the m- or p-position to the substituent represented by the symbol X and at the same time at the m- or p-position of the substituent represented by the symbol Z.

2. A compound according to claim 1, wherein the substituted ureido group is present at the m-position to the substituent represented by the symbol X and at the same time at the p-position to the substituent represented by the symbol Z.

3. A compound according to claim 1, wherein the substituted ureido group is present at the p-position to the substituent represented by the symbol X and at the same time at the m-position to the substituent represented by the symbol Z.

4. A compound according to claim 3, wherein A is a methyl group or a methoxy group, X is a hydrogen atom, Y is an oxygen atom and Z is a methylene group.

5. A compound according to claim 3, wherein A is a methyl group or a methoxy group, X is a hydrogen atom, Y is an oxygen atom and Z is a 1-methyltrimethylene group ($-CH(CH_3)CH_2CH_2-$).

6. A compound according to claim 3, wherein A is a methyl group or a methoxy group, R is a trifluoromethyl group at the m-position to the substituent represented by the symbol Y, X is a hydrogen atom, Y is an oxygen atom, Z is a methylene group and n is 1.

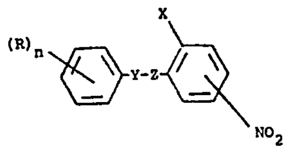
7. A compound according to claim 3, wherein A is a methyl group or a methoxy group, R is a chlorine atom at the m-position to the substituent represented by the symbol Y, X is a hydrogen atom, Y is an oxygen atom, Z is a methylene group and n is an integer of 1.

8. A compound according to claim 3, wherein A is a methyl group or a methoxy group, Rs are chlorine atoms at the m- and p-positions to the substituent represented by the symbol Y, X is a hydrogen atom, Y is an oxygen atom, Z is a methylene group and n is an integer of 2.

9. A compound according to claim 3, wherein A is a methyl group or a methoxy group, R is a hydrogen atom, X is a hydrogen atom, Y is an oxygen atom, Z is a 1-methyltrimethylene group ($-CH(CH_3)CH_2CH_2-$) and n is an integer of 1.

10. Any one of compounds 1 to 87 as defined herein.

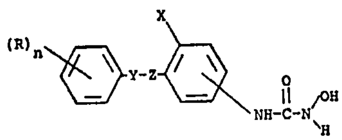
11. A compound of the formula:



(VII)

wherein R, n, Y, Z and X are each as defined in claim 1.

12. A compound of the formula:

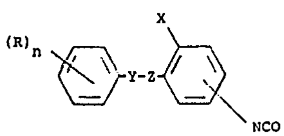


wherein R, n, Y, Z and X are each as defined in claim 1, provided that the substituted ureido group is present at the m- or p-position to the substituent represented by the symbol X and at the same time at the m- or p-position to the substituent represented by the symbol Z.

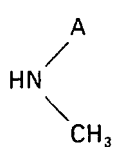
13. A compound according to claim 11, wherein the substituted ureido group is present at the m-position to the substituent represented by the symbol X and at the same time at the p-position to the substituent represented by the symbol Z.

14. A compound as claimed in claim 11 or claim 12 and substantially as hereinbefore described.

15. A process for preparing a compound as claims in claim 1, which comprises reacting a compound of the formula:

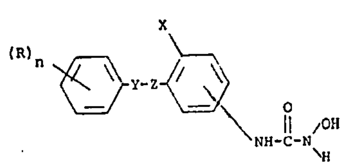


wherein R, X, Y, Z and n are each as defined in claim 1, with a reagent of the formula:



wherein A is as defined in claim 1.

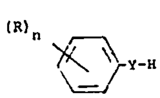
16. A process for preparing a compound as claimed in claim 1 wherein A is a methoxy group, which comprises reacting a compound of the formula:



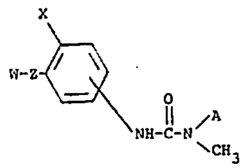
wherein R, X, Y, Z and n are each as defined in claim 1, with a methylating agent.

17. A process according to claim 14, wherein the reaction is carried out in the present of a phase transfer catalyst.

18. A process for preparing a compound as claimed in claim 1 which comprises reacting a compound of the formula:

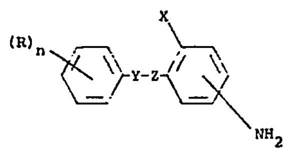


wherein R, Y and n are each as defined in claim 1, with a compound of the formula:



wherein W is a halogen atom, and A, X and Z are each as defined in claim 1.

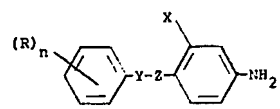
19. A process for preparing a compound as claimed in claim 1, which comprises reacting a compound of the formula:



wherein R, X, Y, Z and n are each as defined in claim 1, with methyl isocyanate, N,N-dimethylcarbamyl halide or N-methoxy-N-methylcarbamyl halide.

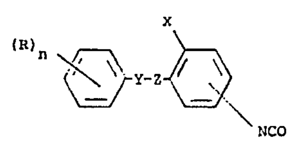
20. A process for preparing a compound as claimed in claim 1 substantially as hereinbefore described in any one of Examples 1 to 8.

21. A process for preparing a compound as claimed in claim 10, which comprises reacting a compound of the formula:



wherein R, X, Y, Z and n are each as defined in claim 10, with phosgene.

22. A process for preparing a compound as claimed in claim 11, which comprises reacting a compound of the formula:



wherein R, X, Y, Z and n are each as defined in claim 11, with hydroxylamine.

23. A herbicidal and/or fungicidal composition which comprises a compound as claimed in any one of claims 1 to 10 together with a carrier or diluent.

24. A composition as claimed in claim 23, wherein the concentration of the active ingredient is from about 1 to 100% by weight.

25. A composition substantially as hereinbefore described in any one of preparation examples 1 to 8.

26. A method for controlling or preventing the growth of weeds or fungi, which comprises applying to the weeds or fungi or to a substrate on which their growth is to be prevented, a compound as claimed in any one of claims 1 to 10, or a composition as claimed in any one of claims 23 to 25.

27. A method for selectively combating weeds or fungi in the cultivation of soybeans or gramineous crops, which comprises applying a compound according to any one of claims 1 to 10 or a composition as claimed in any one of claims 23 to 25 to the area wherein the soybean or gramineous crops are cultivated.

28. Use of the compound according to claim 1 as a herbicide and/or fungicide.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon) Ltd.—1979.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.